

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)**SciVerse ScienceDirect**

Procedia Materials Science 1 (2012) 389 – 396

**Procedia**  
Materials Science[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)11<sup>th</sup> International Congress on Metallurgy & Materials SAM/CONAMET 2011.

## Influence of different oxides on the viscosity of fluorine-free mold fluxes

E. Benavidez\*, L. Santini, M. Valentini, E. Brandaleze

*Metallurgy Department & DEYTEMA - Facultad Regional San Nicolás (UTN), Colon 332, San Nicolás B2900LWH, Argentina*

---

### Abstract

Mold fluxes play an important role in the steel continuous casting process. Mainly, they must prove adequate lubrication between the solidified steel shell and the copper mold. Thus, the knowledge of mold flux viscosity with the temperature is a relevant property for industry applications in order to prevent operation problems and product defects. On the other hand, for environmental reasons, the replacement of fluorine by non-pollutants compounds, is one of the objectives in the design of new compositions for these slags.

In this paper, the viscosity is calculated in the range: 1250-1400 °C applying two models based on their chemical composition and another one using the differential thermal analysis technique. The results obtained with this model showed a good correlation with respect to other traditional models using the chemical composition of the mold flux to estimate the viscosity. The aim is to observe the effect of different oxides on the viscosity of mold fluxes. One of the mold powders was designed with a chemical composition similar to a commercial one (containing 10 wt% of fluorine), while the others powders were fluorine-free (containing boron and lithium). It should be noted that a fluorine-free powder with a viscosity similar to the powder with fluorine was produced replacing 10 wt% fluorine by 4 wt% Li<sub>2</sub>O and 6 wt% B<sub>2</sub>O<sub>3</sub>.

© 2012 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of SAM/CONAMET 2011, Rosario, Argentina. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

**Keywords:** mold fluxes; viscosity; thermal analysis.

---

---

\* Corresponding author. Tel.: +54-3461-420830; fax: +54-3461-420820.  
E-mail address: [ebenavidez@frsn.utn.edu.ar](mailto:ebenavidez@frsn.utn.edu.ar).

## 1. Introduction

In metallurgical processes, high temperature physical properties of the materials have to be taken into account. Particularly, in the steel continuous casting process (CC), a mixture of synthetic slags that contain carbonaceous compounds -named mold fluxes- is continuously added on top of the mold covering the free surface of the liquid steel. At process conditions, a layer of the mold flux is sintered, but the flux (in direct contact with the liquid steel) melts and infiltrates into the gap between the steel shell and the copper mold wall [Branion, 1986]. This layer, solidifies against the mold wall to form an interface consisting of two layers: a glass-solid layer (1-2 mm in thickness) and a liquid one (0.1-0.3 mm in thickness). Simultaneously, the mold oscillates up and down to avoid the steel sticking to the mold and pumps the liquid slag into the gap.

The mold flux layer develops important functions in the CC process, mainly to provide adequate lubrication between the steel and the mold. The presence of longitudinal cracks and star type defects has been associated to inappropriate lubrication [Billany et al., 1991]. Thus, to avoid surface defects and/or breakouts during steel continuous casting process it is necessary that, during solidification of the steel, the mold flux presents both adequate lubrication and uniform heat extraction. The lubrication depends on several process parameters and on the viscosity ( $\eta$ ) of the melted mold powder. The  $\eta$  values must be adjusted to provide a minimum friction and thus avoid the risk of sticking. Therefore, for industrial applications the viscosity values of mold flux at temperatures between 1200-1400 °C are considered to be relevant.

In the last years, the study of mold flux viscosity has focused on the development of new models based on greater quantity of experimental data [Persson et al., 2007; Sukenaga et al., 2006; Simizu et al., 2006; Zhang et al., 2008; Hanao et al., 2006]. However, viscosity measurements at high temperatures are performed using the rotating cylinder method, which is a time-consuming method and demands a certain experimental training. A simpler method to estimate the viscosity of mold fluxes was developed by Mills et al., 1997. In this technique the mold flux is melted and poured on an inclined plane, and then the length of the obtained layer is measured. The length of the layer correlates with the fluidity (inverse of viscosity) of the mold flux. On the other hand, several models based on chemical composition have been developed for predicting mold flux viscosity [Riboud et al., 1981; Watanabe et al., 2000; Koyama et al., 1987; Kim et al., 1992; Iida, 2000]. A revision of these models [Mills et al., 2001] showed that the difference between  $\eta$  values measured experimentally and calculated by both the Iida and the Riboud models ranged between 25 and 30 %.

Fluorine (F) plays an important role because it adjusts the physicochemical properties at high temperatures. However, for environmental care it is necessary to decrease or eliminate the F content in these materials due to the fluoride gases formed by the contact between the mold flux and the molten steel. With this objective several attempts to replace the fluorine in the mold flux composition are recorded. For example, Fox et al., 2005, studied the  $B_2O_3$  and the  $Na_2O$  as substitutes of F in a mold flux used in the CC of billets. In other work, Wen et al., 2007, developed fluorine-free fluxes using  $B_2O_3$ ,  $Na_2O$ ,  $TiO_2$ , and  $Li_2O$  attaining an adequate viscosity to cast peritectic steels. On the other hand, Bezerra et al., 2006, designed a fluorine-free mold flux, with a high basicity, achieving adequate values of viscosity, thermal conductivity, and crystallization grade, adding about 30 wt% of  $B_2O_3$ . In a more recent work, He et al., 2009, designed fluorine-free mold fluxes changing the ratio among oxides in the  $CaO-SiO_2-Na_2O$  system.

In the present work an estimate of viscosity at high temperatures (Moynihan method) based on differential thermal analysis (DTA) data was carried out. The results, obtained by this method, showed a good correlation with the  $\eta$  values obtained through the Riboud and Iida models that calculate the mold fluxes viscosity from the chemical composition. The possibility to estimate the viscosity at high temperatures from a single calorimetric curve -without any information of the chemical composition of mold flux- is a novel method used in the present work.

## 2. Experimental

Four powders with different compositions were prepared. One containing fluorine and the others without F. The powder with F was designed similar to a commercial one containing 10 wt% fluorine (powder 10F). The others three powders were designed replacing the fluoride compound by boron and lithium oxides. In one of them, the fluorine was replaced fully by boron oxide (powder 10B), while in the other two powders the F was replaced by two oxides. For this reason one powder was prepared with boron and a higher percentage of sodium (powder 6B) while in the other one boron and lithium were used (powder 4L). In all compositions the binary basicity index ( $BI = CaO/Si_2O$ ) was maintained at about 0.85.

All powders were prepared by milling/mixing in a ball milling for two hours. Depending on each composition different raw materials were employed: quartz ( $SiO_2$ ), calcium carbonate ( $CaCO_3$ ), sodium carbonate ( $Na_2CO_3$ ), dolomite ( $CaMg(CO_3)_2$ ), sodium feldspars ( $NaAlSi_3O_8$ ), and wollastonite ( $CaSiO_3$ ), adding lithium carbonate ( $Li_2CO_3$ ), borax anhydrous ( $Na_2B_4O_7$ ), and fluorspars ( $CaF_2$ ) as sources of lithium, (Li), boron (B), and fluorine (F), respectively.

The chemical composition (in wt%) of the mold fluxes selected in this study is listed in Table 1.

Table 1. Chemical composition of mold fluxes.

Powder	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	F	B <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	K <sub>2</sub> O
10F	37.0	30.5	1.3	5.4	12.6	9.5	-	-	3.4	0.1	0.1
10B	36.5	31.2	1.3	5.1	12.3	-	9.8	-	3.6	0.1	0.1
6B	34.5	29.6	1.4	5.0	19.6	-	5.8	-	3.9	0.1	0.1
4L	33.2	28.6	1.4	4.7	18.6	-	5.8	3.9	3.7	0.1	0.1

A mass of 10 g of each powder was placed in a graphite crucible and melted at 1300 °C in air. The melted flux was maintained at this temperature for 15 min in order to achieve homogeneity. Then, the melt was fast cooled (quenched) by pouring it onto an inclined stainless steel plane. By this technique, named inclined plane test [Mills, et al., 1997], solid glass layers of approximately 25 mm<sup>2</sup> in section and 150 mm in length were obtained. The length (L) of each layer was measured to have an estimation of the fluidity of each sample. In this case, the inverse of the length (1/L) is proportional to viscosity of material (at 1300°C). Then, the layers were sectioned in bars of 10-15 mm in length. These bars were milled in an agate mortar to produce a glass powder which was assayed in a DTA instrument (DTG-60H - Shimadzu). The DTA runs were performed under a constant heating rate of 10 °C/min, in air.

## 3. Theory

From a single DTA (or DSC) measurement, Moynihan, 1993, proposed a method for estimating the viscosity versus temperature curve. The author showed that the initial and final temperatures, corresponding to the glass transition determined by DTA or DSC, occur at approximately the same viscosity values for every glass (under the same heating rate). Assuming that at very high temperatures the viscosity approximates at the same value for all liquids, the following viscosity expression (Eq.1), for a heating rate of 10 °C/min was deduced:

$$\log \eta = -5 + \frac{14.2}{\left[0.147(T - T_g)/(T_g)^2 \cdot \Delta(1/T_g)\right] + 1} \quad (1)$$

where  $\eta$  is the viscosity in Pa.s,  $T$  is the temperature in kelvin,  $T_g$  is the glass transformation temperature,  $T_g$  is the end point (final temperature) of the glass transition, and  $\Delta(1/T_g)$  is equal to  $(1/T_g - 1/T_g)$ . The simplicity of this method provides a very useful tool to estimate the viscosity of a melt from a single DTA or DSC measurement.

It is important to note that the Riboud model [Riboud et al., 1981] is widely used for mold flux viscosity predictions in the industry. This model permits to evaluate the mold flux viscosity from its chemical composition according to the following equation (Eq.2):

$$\eta = A.T.\exp\left(\frac{B}{T}\right) \quad (2)$$

where  $T$  is temperature in kelvin,  $A$  and  $B$  are parameters which are given by:

$$A = \exp\left[-19.81 + 1.73(X_{CaO} + X_{MnO} + X_{MgO} + X_{FeO} + X_{B_2O_3}) + 5.82(X_{CaF_2}) + 7.02(X_{Na_2O} + X_{K_2O} + X_{Li_2O}) - 35.76(X_{Al_2O_3})\right]$$

$$B = 31140 - 23896(X_{CaO} + X_{MnO} + X_{MgO} + X_{FeO} + X_{B_2O_3}) - 46356(X_{CaF_2}) - 39159(X_{Na_2O} + X_{K_2O} + X_{Li_2O}) + 68833(X_{Al_2O_3})$$

where  $X_i$  is the molar fraction of the  $i$ -compound.

The Iida model [Iida et al., 2000; Iida, 2002] also predicts the viscosity of different types of slags from their chemical compositions. In this model, the viscosity equation is expressed by Eq.3 [Iida, 2002]:

$$\eta = A.\eta_0.\exp\left(\frac{E}{B_i}\right) \quad (3)$$

where  $A$  and  $E$  are the parameters determined to best fit experimental data:

$$A = 1.029 - 2.078 \times 10^{-3} \cdot T + 1.050 \times 10^{-6} \cdot T^2$$

$$E = 28.460 - 2.0884 \times 10^{-2} \cdot T + 4.000 \times 10^{-6} \cdot T^2$$

where  $\eta_0$  is the viscosity of non-network forming melts:

$$\eta_0 = \sum_{i=1}^n \eta_{0i} \cdot X_i$$

and  $B_i$  is the modified basicity index:

$$B_i = \frac{\sum (\alpha_i \cdot W_i)_B + \alpha_{Fe_2O_3} \cdot W_{Fe_2O_3}}{\sum (\alpha_i \cdot W_i)_A + \alpha_{Al_2O_3} \cdot W_{Al_2O_3} + \alpha_{TiO_2} \cdot W_{TiO_2}}$$

In this case,  $\alpha$  is the specific coefficient and  $W$  is the mass percentage. The subscripts  $A$  and  $B$  represent the acidic and basic oxides or components, respectively.

#### 4. Results and discussion

Figure 1 shows the DTA curve in the glass transition region of powder 10F. From this curve, the values  $T_g = 490^\circ\text{C}$  and  $T'_g = 533^\circ\text{C}$  were determined.

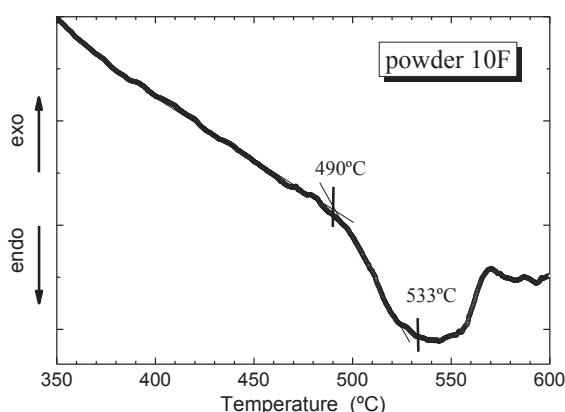


Fig. 1. Glass transition region of powder 10F.

$T_g$  and  $T'_g$  corresponding to the four samples were determined applying the same methodology (see Table 2). The inverse of layer length ( $1/L$ ) and the binary basicity index ( $BI = \text{CaO}/\text{Si}_2\text{O}$ ) of each flux are listed in this table.

Table 2. Values of  $T_g$ ,  $T'_g$ ,  $1/L$  and  $BI$  corresponding to different samples.

	10F	10B	6B	4L
$T_g$	$490^\circ\text{C}$	$572^\circ\text{C}$	$539^\circ\text{C}$	$455^\circ\text{C}$
$T'_g$	$533^\circ\text{C}$	$614^\circ\text{C}$	$581^\circ\text{C}$	$500^\circ\text{C}$
$1/L$	$5.52\text{ m}^{-1}$	$9.80\text{ m}^{-1}$	$8.06\text{ m}^{-1}$	$5.62\text{ m}^{-1}$
$BI$	0.82	0.85	0.86	0.86

It is observed that, in all cases, the interval of the glass transition ( $T_g - T'_g$ ) is  $42\text{--}45^\circ\text{C}$ .

Data from Table 2 were used in the Moynihan model (Eq.1) to estimate the viscosity in the range of interest to mold fluxes:  $1250\text{--}1400^\circ\text{C}$ . At this point, it is important to mention that, at temperatures lower than  $1200^\circ\text{C}$ , the viscosity increases dramatically and its behavior is non-newtonian. This point is named break temperature ( $T_{\text{break}}$ ). This temperature represents the point at which the first solid crystals begin to precipitate in the melt [Sridhar et al., 2000]. To the most of mold fluxes  $T_{\text{break}}$  ranges between  $1100\text{--}1200^\circ\text{C}$ . Thus, the estimation of the viscosity at lower temperatures than  $1200^\circ\text{C}$  has not practical interest.

Figures 2-4 show the viscosity vs temperature curves obtained by the different methods: Riboud (Fig.2), Iida (Fig.3), and Moynihan (Fig.4).

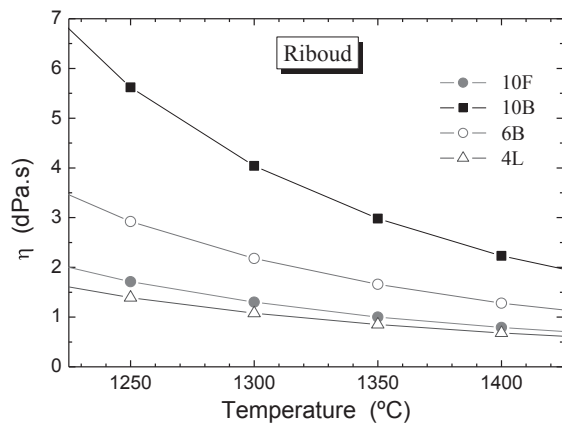


Fig. 2. Viscosity of samples obtained by the Riboud model.

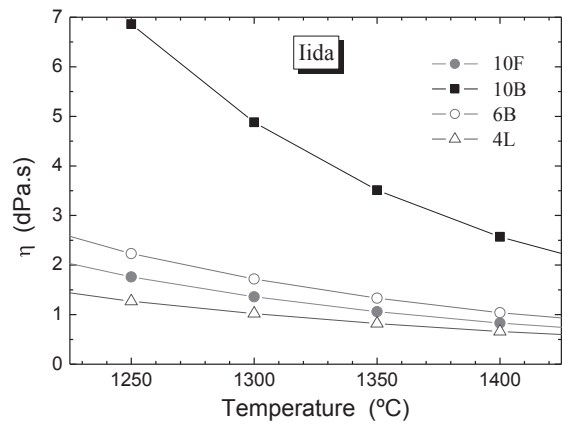


Fig. 3. Viscosity of samples obtained by the Lida model.

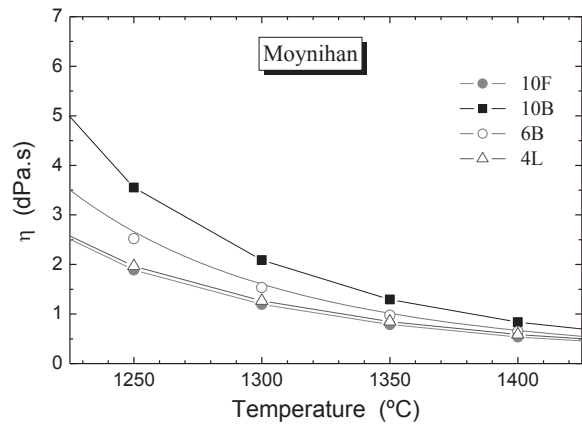


Fig. 4. Viscosity of samples obtained by the Moynihan model.

Comparing the  $\eta$ -values obtained by Riboud and Iida models, the differences between them are lesser in powders 10F (< 6 %) and 4L (< 8 %), while in powders 10B and 6B this difference is (in average) about 20%. The estimation of error in the  $\eta$ -values obtained by the Moynihan model was  $\cong$  15 %. This error comes from the determination of  $T_g$  and  $T_g'$  values from DTA curves.

In the studied range of temperature, the Iida and Riboud models present the following order of viscosities:  $\eta(10B) > \eta(6B) > \eta(10F) > \eta(4L)$ . On the other hand, according to the Moynihan model, the viscosity values present a similar order, except that  $\eta(10F)$  is slightly lower than  $\eta(4L)$ . According to Moynihan, this order in the viscosity values is similar to that obtained by the  $1/L$  values (inclined plane method), namely:  $1/L(10B) > 1/L(6B) > 1/L(4L) > 1/L(10F)$ . It should be remembered that the inverse of the length of melted layers cooled down from 1300 °C ( $1/L$ ) is associated to the viscosity of material. Accordingly, it is possible to consider that both experimental data: length of the melted layer (inclined plane method) and DTA of the powder obtained from this layer (Moynihan method) allow to estimate and compare, on an experimental way, values of viscosity at high temperatures.

It should be noted that, before designing a mold flux composition, the viscosity is generally estimated by the Riboud model, since it is simpler than the Iida one. However, when the composition of starting raw materials (or mold flux) is unknown, a single run of DTA on quenched material (Moynihan model) proves to be a good alternative to know the viscosity behavior at high temperatures.

It is highlighted that, although it is possible to design a fluorine-free mold flux –applying the Riboud model– with a viscosity very similar to  $\eta$  of powder with fluorine (10F), the limitation imposed by the different raw materials should be taken into account. Namely, the chemical compositions used in the models (Riboud and Iida) are expressed in oxides, while the preparation of mold fluxes starts from raw materials based on carbonates, feldspars, etc. At this point, the ratio  $CaO/SiO_2$  should also be taken into account.

Analysing the data obtained from different models, it is noted that by replacing the totality of fluorine (powder 10F) by 9.8 wt% boron oxide (powder 10B), a large increase in viscosity is produced. So, the single addition of  $B_2O_3$  does not seem a good option to directly replace F. Then, the viscosity is diminished when part of  $B_2O_3$  is replaced by  $Na_2O$ . It is known that sodium oxide decreases the viscosity. However, in this oxide system, increasing the percentage of  $Na_2O$  from 12.5 wt% to 19.5 wt% is not sufficient to attain the viscosity of powder 10F. Finally, the addition of 4 wt%  $Li_2O$  to powder containing 6 wt%  $B_2O_3$  and 19 wt%  $Na_2O$ , results in a mold flux whose viscosity at 1300 °C is similar to the powder 10F (taken into account the errors inherent to the models applied).

Although the data obtained by Moynihan method to estimate the viscosity at high temperatures using glass parameters (such as  $T_g$ ) seem reasonable, it is necessary to verify it experimentally (for example by rotating cylinder method) to validate these tendencies.

## 5. Conclusions

(i) The Moynihan's method was useful to estimate the viscosity of mold fluxes in the range 1250-1400 °C, by a single DTA run, without any knowledge of the mold flux chemical composition. Also, a good correlation was obtained between the viscosity values determined by this method and the viscosity predicted by two traditional models: Riboud and Iida, based on the flux chemical composition.

(ii) Replacing directly 10 wt% F by 10 wt%  $B_2O_3$  caused a strong increase in the viscosity.

(iii) The substitution of 10 wt% F by the addition of 6 wt%  $B_2O_3$  and the increase of the content of  $Na_2O$  ( $\cong$  7 wt%) produced a lowering of viscosity, but insufficient to obtain  $\eta$ -values similar to the flux with 10 wt% F.

(iv) The replacement of fluorine by 4 wt%  $Li_2O$  and 6 wt%  $B_2O_3$ , presented a viscosity versus temperature behavior similar to powder with 10 wt% F, showing the important role of lithium to increase the fluidity in these slags.

## Acknowledgements

The authors acknowledge the financial support of the Universidad Tecnológica Nacional, Argentina. It is thanks the critical reading of this work by Dr. C.J.R. González Oliver (Centro Atómico Bariloche, Argentina).

## References

- Bezerra, C., Valadares, C., Rocha, I.P., Bolota, J., Carboni, M., Scripnic, I., Santos, C. Mills, K.C., Lever, D., 2006. "Impact of Fluorine free Mold Flux Used on Continuous Casting Process", XXXVII Steelmaking Seminar ABM. Porto Alegre, Brazil, p.359.
- Billany, T.J.H., Normanton, A.S., Mills, K.C., Grieveson, P., 1991. Surface Cracking in Continuously Cast Products, *Ironmaking and Steelmaking* 18, p. 403.
- Branion, V., 1986. Mould Fluxes for Continuous Casting; *Iron and Steelmaker* 13, p. 41.
- Fox, A.B., Mills, K.C., Lever, D., Bezerra, C., Valadares, C., Unamuno, I., Laraudogoitia, J.J., Gisby, J., 2005. Development of Fluoride-Free Fluxes for Billet Casting, *ISIJ International* 45, p. 1051.
- Hanao, M., Kawamoto, M., Tanaka, T., Nakamoto, H., 2006. Evaluation of Viscosity of Mold Flux by Using Neural Network Computation, *ISIJ International* 46, p.346.
- He, S., Wang, Q., Xie, D., Xu, C., Li, Z.S., Mills, K.C., 2009. Solidification and Crystallization Properties of CaO-SiO<sub>2</sub>-Na<sub>2</sub>O Based Mold Fluxes, *International Journal of Minerals, Metallurgy and Materials* 16, p.261.
- Iida, T., 2000. Accurate Prediction of the Viscosities of Various Industrial Slags from Chemical Composition, *J. High Temperature Soc.* 25, p.93.
- Iida, T., 2002. "A Model for Accurate Viscosity Predictions of Various Types of Molten Slags and Glasses", *Proceedings of the Ken Mills Symposium*. London, UK, p. 101.
- Iida, T., Sakai, H., Kita, Y., Shigeno, K., 2000. An Equation for Accurate Prediction of the Viscosities of Blast Furnace Type Slags from Chemical Composition, *ISIJ International* 40, p. S110.
- Kim, J.W., Choi, J., Kwon, O.H., Lee, I.R., Shin, Y.K., Park, J.S., 1992. "Viscous characteristics of synthetic mold powder for high speed continuous casting", *Proc. 4<sup>th</sup> International Conference on Molten Slags and Fluxes*. Sendai, Japan, p.468.
- Koyama, K., Nagano, K., Nagano, Y., Nakano, T., 1987. Design for Chemical and Physical Properties of Continuous Casting Powders, *Nippon Steel Tech. Rep.* 34, p.41.
- Mills, K. C., Halali, M., Lörz, H.P., Kinder, A., Pomfret, R., Walker, B., 1997, "A Simple Test for the Measurement of Slag Viscosities", *5<sup>th</sup> International Conference on Molten Slags, Fluxes and Salts '97*. Sydney, Australia, p. 535.
- Mills, K.C., Chapman, L., Fox, A.B., Sridhar, S., 2001. Round Robin Program for Slag Viscosity Estimation, *Scand. J. Metallurgy* 30, p.396.
- Moynihan C.T., 1993. Correlation between the width of the glass transition region and the temperature dependence of the viscosity of high-Tg glasses, *J. Am. Ceram. Soc.* 76, p.1081.
- Persson, M., Gonnerup, M., Seetharaman S., 2007. Kinetic Studies of Fluoride Evaporation from Slags, *ISIJ International* 47, p. 1711.
- Riboud, P.V., Roux, Y., Lucas, L.D., Gaye, H., 1981. Improvement of Continuous Casting Powders, *Fachberichte Huttenpraxis Metallweiterverarbeitung* 19, p.859.
- Shimizu, F., Tokunaga, H., Saito, N., Nakashima, K., 2006. Viscosity and Surface Tension Measurements of RE<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub> (RE=Y, Gd, Nd and La) melts, *ISIJ International* 3, p.388.
- Sridhar, S., Mills, K.C., Afrange, O.D.C., Lörz, H.P., Carli, R., 2000. Break Temperatures of Mould Fluxes and Their Relevance to Continuous Casting, *Ironmaking and Steelmaking* 27, p. 238.
- Sukenaga, S., Saito, N., Kawakami, K., Nakashima, K., 2006. Viscosities of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-(R<sub>2</sub>O or RO) Melts, *ISIJ International* 46, p. 352.
- Watanabe, T., Fukuyama, H., Nagata, K. Susa, M., 2000. Phase diagram cuspidine (3CaO-2SiO<sub>2</sub>-CaF<sub>2</sub>)-CaF<sub>2</sub>, *Metallurgical and Materials Transactions B* 31, p.1273.
- Wen, G., Sridhar, S., Tang, P., Qi, X., Liu, Y., 2007. Development of Fluoride-free Mold Powders for Peritectic Steel Slab Casting, *ISIJ International* 47, p. 1117.
- Zhang, Z., Wen, G., Tan, P., Sridhar, S., 2008. The Influence of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> Ratio on the Viscosity of Mold Fluxes, *ISIJ International* 48, p.739.